

# Polymer microstructure studies using soft X-ray spectromicroscopy

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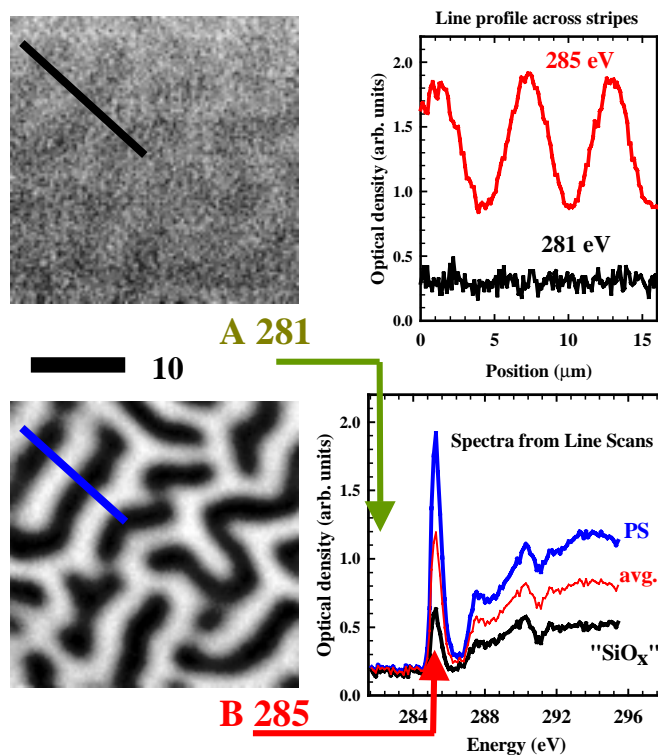
## INTRODUCTION

There are many interesting problems in polymer physics and chemistry that require detailed and quantitative chemical analysis (speciation) at the sub-micron spatial scale. These include issues such as: the chemical basis of phase segregation; determination of the morphology and interface chemistry of blends and co-polymer systems; mechanisms of formation and structure of 'self-assembled' nano-patterned structures. This document describes recent studies of some fundamental aspects of polymer microstructure using the ALS BL 7.0.1 scanning transmission X-ray microscope (STXM), both to report on the science and to provide an indication of the quality of the images and spectroscopy that can now be achieved.

## SELF-ORGANIZATION OF CONFINED, FREE STANDING POLYMER FILMS

Patterning of thin polymer films is attracting increasing interest, both from a fundamental point of view, and on account of potential technological applications. However the thermal stability of these films can be a limitation on account of hole formation driven by dispersion forces which amplify structural instabilities at the film surface. Mechanical confinement of polymer films offers the possibility of control over this instability which in turn raises possibilities for unique self-assemblies of polymers on surfaces patterned on submicron length scales. We have used STXM to study very thin (~50 nm prior to annealing) polystyrene films confined between thin continuous layers of silicon oxide. The SiO<sub>x</sub> layers prevent hole formation. However aggressive annealing at temperatures well above T<sub>g</sub> generates a novel in-plane structure driven by the attractive dispersion force between the SiO<sub>x</sub>-air surface [1]. These structures offer an attractive test-bed for understanding and developing control mechanisms for one of the fundamental forces governing self-assembly of polymer structures.

In order to fully model the mechanisms for this spontaneously generated lateral morphology, it is important to measure the thickness of the trapped polymer film throughout the structure. The optical density (OD) obtained from STXM readily provides

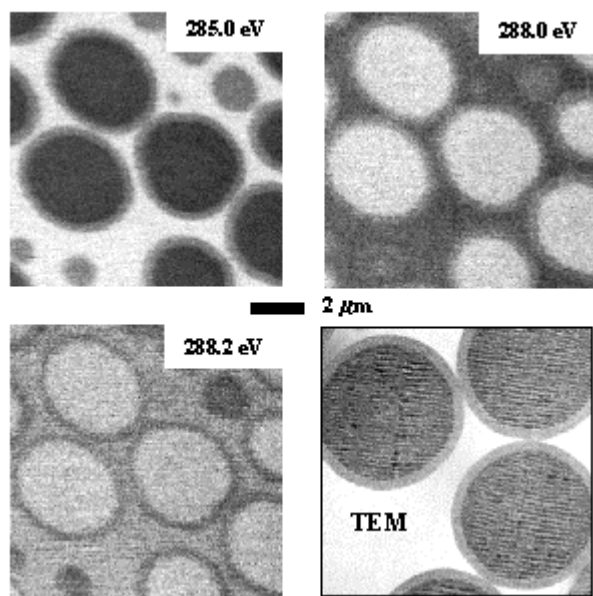


**Figure 1.** Images and spectra of a trilayer structure consisting of a 60 nm film of polystyrene (pS) coated on each side with 30 nm of SiO<sub>x</sub>. Annealing causes the indicated morphology. Profiles and spectra show there is still significant pS in the dark regions.

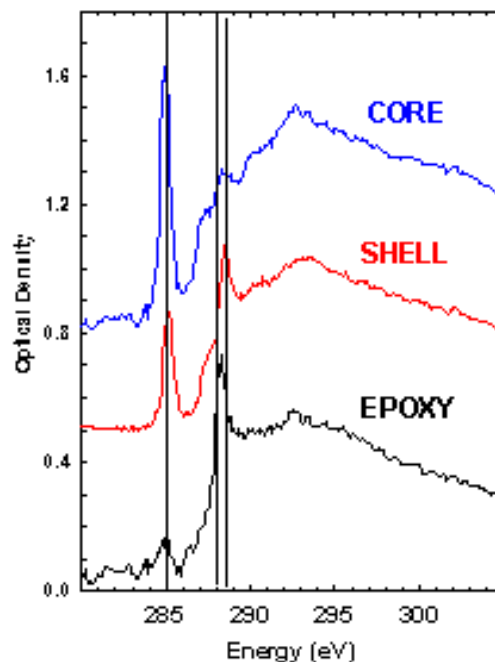
this information. Prior to these measurements it had been assumed that there was almost complete exclusion of the polystyrene from the dark, non-continuous regions. However, STXM indicated ~30% residual PS in those areas (see **Fig. 1**). Further investigation of trapped thin film polymers of materials with different strengths of interaction with  $\text{SiO}_x$  are planned.

## MICROSTRUCTURE OF LATEX PARTICLES

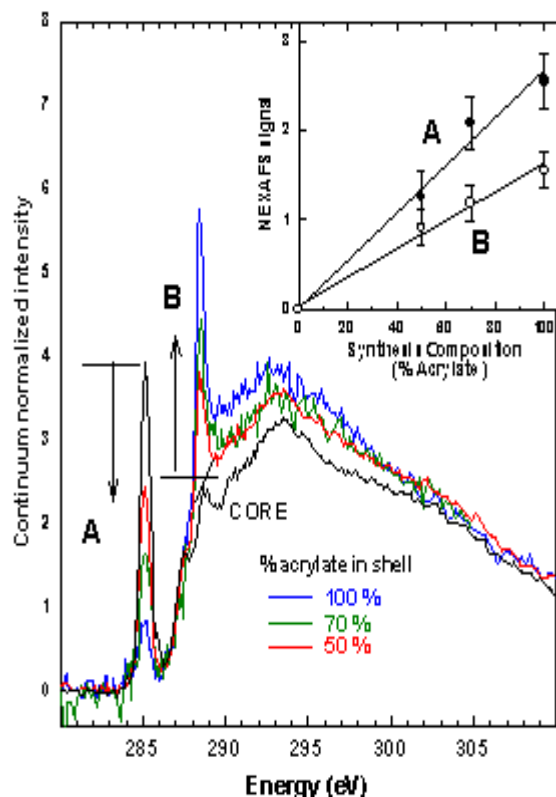
Latex particles with internal structure are attractive for a number of applications, including coatings, adhesives, chemical delivery and separation science [2]. In order to optimize these structures for particular applications (e.g. pheromone delivery for environmentally benign, controlled release pest management; highly selective affinity separation resins and catalysts) it is important to be able to visualize their internal structure, determine its origin, and chemically analyze (speciate) the composition of various structural components. While transmission electron microscopy (TEM) of cross-sections of latex spheres readily reveals the presence or absence of internal structure of few micron sized latex particles, the limited chemical sensitivity of TEM means that one cannot be sure if the observed structure arises from a genuine chemical difference in the various regions (e.g. core versus shell) or whether it is a consequence of a density and/or thickness variation (perhaps driven by some underlying chemical difference). STXM images at a range of photon energies provide a means to quantify the relative contributions of chemical versus density/thickness contrast. **Fig 2** shows examples of a current study of crosslinked acrylic-polystyrene latex particles which have been synthesized in a two-step process to intentionally segregate all of the poly-acrylate (pA) component to the shell region. There are three levels of contrast reversal. The spectral basis for this can be ascertained from comparison of the spectra of the polystyrene (pS) core, the pS-pA shell, and the epoxy support material (**Fig. 3**).



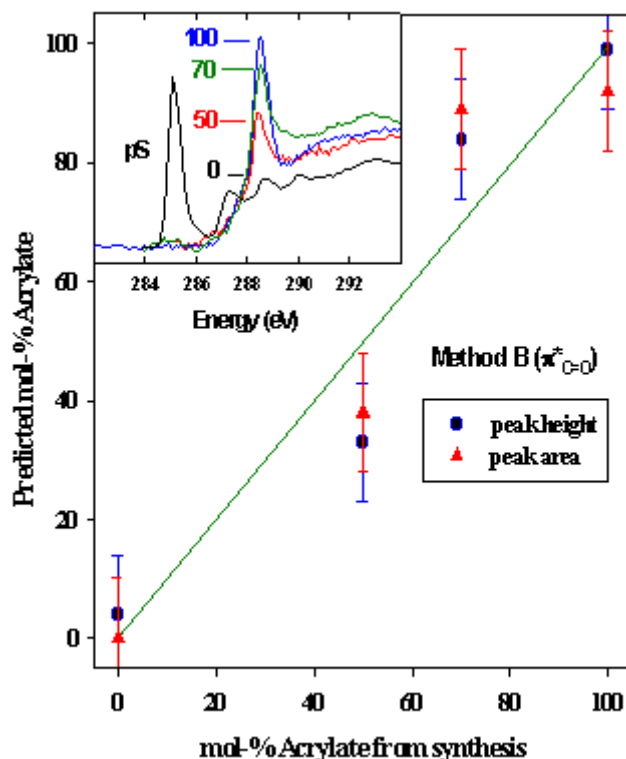
**Figure 2.** Selected energy STXM images of a styrene-based core-shell latex sample containing 70% poly-acrylate in the shell region. The energies of each image, and thus the origin of the dramatic changes in chemical contrast, are indicated in the next figure. The lower right image is a bright field electron micrograph for comparison.



**Figure 3.** C 1s NEXAFS spectra of the three chemical components in the styrene-based core-shell latex sample with 70% poly-acrylate in the shell. The vertical lines indicate the energies of the STXM images presented in the preceding figure.



**Figure 4.** Normalized C 1s spectra of the shell region of styrene-acrylate latex particles of different composition. The insert plots the compositional dependence of the heights of the styrene and acrylate  $\pi^*$  peak signals.



**Figure 5** Amount (mol-%) of acrylate in the shell region, determined from the acrylate NEXAFS signal, plotted versus the synthesis composition. The insert shows the acrylate signal, isolated by subtracting the spectrum of pure polystyrene from each shell spectrum.

In order to test our ability to quantify internal chemical composition in latex systems, a number of preparations with systematic variation of the composition of the  $\sim 0.8 \mu\text{m}$  shell region were examined. **Fig. 4** compares C 1s spectra of the shell region of samples with 50%, 70% and 100% acrylate in the shell, extracted from line-scans across several particles. The shell composition was determined from both the styrene  $\pi^*(\text{C}=\text{C})$  signal at 285 eV (method-A) and the acrylate  $\pi^*(\text{C}=\text{O})$  signal at 288 eV (method-B). **Fig. 5** plots the mol-% poly-acrylate determined from the method-B approach (both peak height and peak area), in comparison with the compositions predicted from the synthetic methodology. The agreement is reasonable, but there are still significant deviations. Study of a larger number of samples and development of a more precise means of extracting the shell signal, to the exclusion of the core and matrix signals, is expected to lead to significant improvements over the level of quantitation accuracy shown in Fig. 5. That study is in progress.

A more challenging goal for polymer STXM is the study of spontaneous internal organization of latex particles, either in the synthesis, or from subsequent modification (e.g. loading with other species, time evolution of a loaded particle, etc.). **Fig 6** compares TEM and STXM images of an interesting latex particle sample which shows a ‘tree-ring’ morphology. While electron microscopy reveals this internal morphology, it is unclear from the TEM work whether the ring pattern arises from simple density / thickness variations, or whether it is the result of chemical

inhomogeneity. The observation of the ‘tree-ring’ morphology only at specific photon energies in the STXM study clearly points to a strong chemical compositional origin of this morphology. From this observation we believe that the tree-ring structure is most likely generated by heterogeneous chemical oscillations in the one-step synthesis used to prepare this sample.

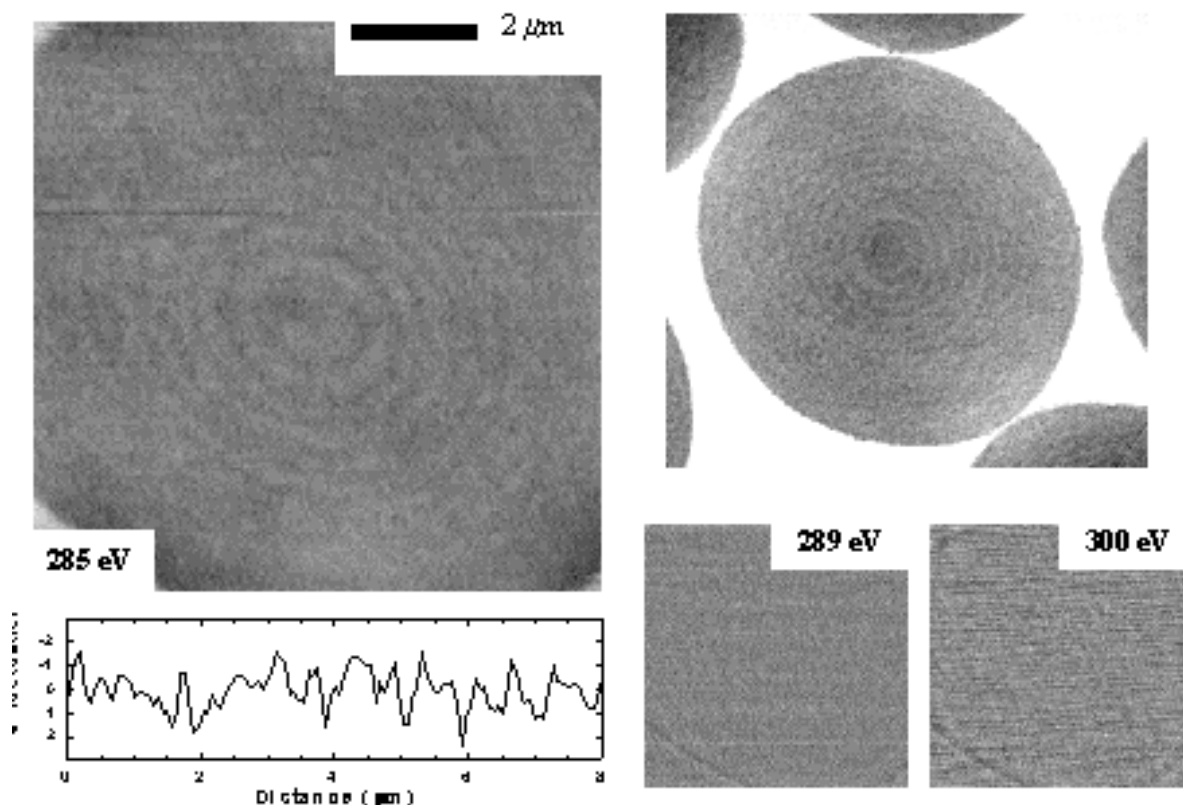
## ACKNOWLEDGEMENTS

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**Figure 6.** Selected energy STXM images of a latex particle prepared by a single step synthesis. A ‘tree-ring’ structure is detected in the STXM image recorded at 285 eV, and by TEM (upper right). The diminution of the ‘tree ring’ structure in images at other energies (lower right) indicates it is associated with variable composition. It is likely this arises from chemical oscillations in the polymerization of the mixed, styrene, chloro-styrene system. The intensity profile across the particle (lower left) indicates that the chemical variation responsible for the ring structure involves only a few % compositional change.